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CERTIFICATE

This certificate is issued in support of an application for Patent registration in a country outside New Zealand pursuant to the Patents Act 1953 and the Regulations thereunder.

I hereby certify that annexed is a true copy of the Provisional Specification as filed on 13 September 2002 with an application for Letters Patent number 521407 made by KLEIN MEDICAL LIMITED.

PRIORITY DOCUMENT
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Dated 29 September 2003

Neville Harris

Neville Harris
Commissioner of Patents, Trade Marks and Designs

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NEW ZEALAND

330 High Street, Lower Hutt and 17 Toop Street, Seaview
PO Box 30687, Lower Hutt, New Zealand or DX SX 11129, Wellington
Phone: +64 4 560 1600, Fax: +64 4 560 1691, www.iponz.govt.nz

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PATENTS ACT, 1953

PROVISIONAL SPECIFICATION

"Spectrophotometer Detection Apparatus"

We, **KLEIN MEDICAL LIMITED**, a company duly incorporated under the laws of New Zealand of 1/26 Victoria Road, Devonport, Auckland, New Zealand, do hereby declare this invention to be described in the following statement:

FIELD OF INVENTION

The present invention relates to a system for analysing the spectral absorption of a material in a test sample, and in particular to improvements in the system of the type using detection apparatus.

BACKGROUND OF THE INVENTION

The simplest spectroscope splits incident visible light into spectral lines that can be observed by the human eye. In more complicated analysis, for example spectrochemical analysis, the substance under investigation is heated, so that it emits radiation. Each component of the substance emits a characteristic radiation, and this can be used as a means of identification. The radiation is passed through a diffraction grating or a prism to separate it into its constituent wavelengths. Detectors are then used to observe or record details of the spectrum, and instrument can be used to measure the wavelengths and intensities of spectral lines. A permanent record of the results (a spectrograph) may be made to allow more detailed analysis. Comparison of the spectrum with the spectra of known, pure, substances allows the components to be identified and, with quantitative analysis, their relative proportions determined. This offers an extremely sensitive method of analysis of chemical substances, and automated spectroscopic procedures are now used routinely in laboratories.

Most laboratory apparatus are currently used for the measurement of the concentration of a material in a solution are relatively complex in nature. Their degree of complexity is at least partially a cause for several disadvantages:

- they are relatively expensive
- they are often relatively delicate as they use prisms and dispersion gratings and are generally unsuitable for use in the field or in normal manufacturing and processing environments,
- they are generally specific in purpose and often cannot be readily adapted for other applications.

The term 'material' shall be used in its broadest sense and shall typically not only

restricted to pieces of solid matter but also to volumes of liquids. In addition the term 'solution' shall also be taken to include the gaseous phase, but it is envisaged that the preferred embodiment shall be a liquid.

International patent application number WO96/31764 discloses a method and apparatus for the quantitative determination of particles in fluid. This apparatus comprises one or more light emitters, and one or more light detectors sensitive to the output of the emitters. Data is gathered from a plurality of signal paths between the emitter and detector. This data is subsequently evaluated by comparison with known data for different fluid particles in a fluid sample.

United States Patent Number US4,158,505 describes a spectrophotometer consisting of a wideband light source, paths provided for the sample and reference lights, a chopper wheel allowing the sample and reference light to be interspersed with dark period, and be alternately incident on a dispersion grating and thus transmitted onto a linear array of photodiodes.

United States Patent Number US3,955,082 describes a single photodetector for measuring a variety of wavelengths. The single photodetector is constructed from a plurality of detector sections each having a variable bandwidth and controlled by varying the reverse bias voltage.

United States Patent Number US5,357,343 describes a spectrophotometer consisting of a single emitter detector and rotating chopper. The rotary chopper contains filters to select wavelengths to be incident on the detector at anyone time. All the inventions described in each specification possess many of the general disadvantages described previously.

SUMMARY OF INVENTION

It is therefore an object of the present invention to provide a spectrophotometer which goes some way to overcoming the abovementioned disadvantages in the prior art or will at least provide the industry with a useful choice.

Accordingly in the first aspect of the present invention may broadly be said to consist in an analyser for the detection of material in a sample comprising:

a source adapted to provide a broadband signal at said sample with variable intensity depending on an applied control signal,

a detector adapted with variable spectral response depending on an applied control signal and providing an output signal, and

a controller adapted to apply signals to said source and said detector according to predetermined variations in intensity and spectral response and determining a characteristic of said sample based on said output in relation to said variations.

Preferably said control signal applied to said source controls the current.

Preferably said control signal applied to said detector controls the reverse voltage.

Alternately said control signals control individual control means that are adapted to apply control signals to said source and said detector.

Preferably said output signal from said detector is amplified and digitised prior to being supplied to said controller.

Preferably said controller is a microprocessor.

Preferably said detector is a photodiode detector.

Preferably said source is a light emitting diode.

Alternately said source is a tungsten filament lamp.

Accordingly in the second aspect of the present invention may broadly be said to consist in a method of analysing a sample comprising:

transmitting a broadband signal at said sample and varying the intensity of said broadband signal according to predetermined conditions,

detecting a reflected signal from said sample which is detected according to predetermined conditions, and

determining a characteristic of said sample based on at least a plurality of varied broadband signals and varied reflected signals.

This invention may also be said broadly to consist in the parts, elements and features referred to or indicated in the specification of the application, individually or collectively, and any or all combinations of any two or more of said parts, elements or features, and where specific integers are mentioned herein which have known equivalents in the art to which this invention relates, such known equivalents are deemed to be

incorporated herein as if individually set forth.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a block diagram of the overall structure of the present invention;

Figure 2a shows a cross-sectional drawing of the preferred embodiment of the sprectral analysing apparatus of the present invention;

Figure 2b shows a cross-sectional enlarged drawing of the preferred embodiment of the reflection angle through the sample being tested;

Figure 2c shows a cross-sectional enlarged drawing of the preferred embodiment of the chopper wheel in the beam splitting apparatus;

Figure 3a shows a cross-sectional drawing of an alternate embodiment of the spectral analysing apparatus;

Figure 3b shows a plan cross-sectional drawing of the alternate embodiment of the spectral analysing apparatus;

Figure 3c is a section view of the chopping wheel of the alternate embodiment of the spectral analysing apparatus;

Figure 4a illustrates how the photodetector is penetrated by short wavelength photons;

Figure 4b illustrates how the photodetector is penetrated by long wavelength photons;

Figure 5a shows the response of a typical photodetector by varying the intensity of the light source;

Figure 5b shows the response of a typical photodetector by varying the reverse voltage across the photodetector;

Figure 5c shows the response of a typical photodetector by varying both the light intensity and the reverse voltage.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred embodiment of the present invention relates to a spectrophotometer for providing a qualitative and quantitative measure of material size, density and spectral

response of a sample. In particular, the spectrophotometer reads the reflectance of a sample. In an alternate embodiment, the spectrophotometer reads the absorbence of a sample. The preferred embodiment of the apparatus of the present invention will comprise of at least one emitter and at least one detector. Preferably the emitter will be a single broadband light emitter or alternately be comprised of an array of several light emitters that function as if a single light emitter. Preferably the detector will be a standard type photodiode capable of measuring a wide spectrum of frequencies. The emitter and detector are controlled by a microprocessor. This in turn is connected to an external PC.

Referring to Figure 1 the light emitter 1 of the present invention generates radiation over a broad range of frequencies including visible and infrared regions of the electromagnetic spectrum, a broadband signal. Preferred embodiments use inexpensive emitters such as light emitting diodes or tungsten filament lamps. Similarly, a relatively inexpensive light sensitive detector 9 is capable of detecting a broad spectrum of wavelengths is used. This detector 9 preferably uses a photodiode to detect incident light signals. The emitter 1 and detector 9 are both controlled by a controller module 3, preferably a microprocessor. The microprocessor 3 controls the intensity of the light emitted from the emitter 1 by varying the current supply 2. The operation of the detector 9 is controlled by varying the supply of voltage or reverse bias 10. Any signal generated by the detector 9 is amplified and converted into a digital format before being processed by the microprocessor 3.

In order to measure the sample under test, the light from the emitter 1 is split up into separate paths before falling incident on the detector 9. This operation is performed by a device called a beam splitter or a chopping wheel 5. The rotation of the chopping wheel 5 is controlled by the microprocessor 3 so that any one time, the detector 9 will only sense one signal. Typically the chopping wheel 5 blocks the path of other signals while allowing one signal to pass and fall incident on the detector 9. The three signals possible in the preferred embodiment are the reference signal, sample signal and dark signal (no signal).

Figure 2a illustrates the beam splitting apparatus 30 of the present invention. The beam splitting apparatus 30 is comprised of several elements, these include a light source

32, a chopping wheel 33, paths to direct the lights 36, 36a, 37 and 38, a detector 35, and a sample under test 31. The sample under test is typically contained by a test tube 31. Preferably the test tube 31 used is comprised of two diametrically different sections 31a and 31b. The lower section 31b of this test tube 31 has a smaller diameter than the top section 31a to allow for small amounts of a sample to be tested. Alternately a standard test tube may be used, this test tube has a regular diameter for its entire length. The test tube 31 containing the sample is inserted into a holding cavity 50 within the spectrophotometer for measurement.

Figure 2b illustrates the reflection angle of the light from the light source 32 towards the chopper wheel 33, along path 36a. The angle of reflection is substantially 90 degrees so that the reflected light, travelling along path 36a, is perpendicular to the detector 35. This allows for optimum information transfer onto the light detector 35 with a minimum of diffraction distortion.

With reference to Figure 2c, the chopper wheel is comprised of a circular type barrel with one section of the wheel being substantially flat 34. The depth of this flat section 34 is dictated by the diameter of the light transmission pathways 36, 36a, 37 and 38. In the preferred embodiment the depth of the flat section 34 on wheel 33 is substantially the same as the diameter of the light transmission pathways 36, 36a, 37 and 38. Alternately, flat section 34 is approximately half way between the circular edge and the centre of rotation of the chopper wheel 33.

One complete revolution of the chopper wheel 33 will result in any one of three signals being incident on the detector 35. These three signals include a reference signal, a sample signal, and a dark signal. The reference signal is when point 33a on the chopper wheel 33 is at substantially positive 10 degrees from the vertical axis. The information provided at the detector 35 is coming directly from the light source 32. The sample signal is detected when point 33a on the chopper wheel 33 is at substantially at negative 10 degrees from the vertical axis. This information at the detector 33 is comprised of the radiation coming from the reflectance off the sample. At any other time when there is no light incident on the detector 35 is known as the dark current. Dark current is important as it provides information for the calibration of the spectrophotometer. This information

generally relates to the temperature drift of the detector 35 and the associated electronics.

An alternative embodiment of the physical structure of the spectrophotometer is shown in Figures 3a to 3c. Referring to Figure 3a, the angle between the light source 51 and detector 55 as it reflects off sample 50 is approximately 45°. The chopping wheel 56 dictates when the light signal will be incident on the detector 55. In Figure 3c, the chopping wheel 53 is divided into three sections, namely a hole section 62, a mirror section 60 and a black section 61. The hole section 62 allows the signal to reflect off the sample 50 and be detected by the detector 55. The mirror section 60 reflects the signal directly to the detector 55. This results in reference readings. The black section 61 stops the transmission of light signal to the detector 55 so dark current readings may be taken. In this alternative embodiment, the chopping wheel 53 is off to one side of the sample 50. This allows transmission of the signal light through one section of the chopping wheel 53 at any one time, so simplifying the control of the chopping wheel 53.

The detector 35 of the present invention is typically of a *pn*-junction or a *p-i-n* photodiode type. Referring to Figures 4a and 4b, the photodetector 35 is connected in reverse bias with a DC voltage source 68, in particular the negative battery terminal is connected to the *p*-side 65 of the diode 35 and the positive terminal is connected to the *n*-side 67 of the diode 35.

The operation of the detector 35 as it relates to the present invention will now be explained. When a photon of light is absorbed by the detector 35 it excites an electron and produces a single pair of charge carriers, an electron and a hole, where a hole is simply the absence of an electron in the diodes semiconductor lattice. Current passes through the semiconductor when the charge carriers separate and move in opposite directions. The detector 35 collects the photon-induced charge carriers that can be measured as current or voltage at its electrodes.

An *n*-type 67 semiconductor material is preferably doped with Silicon or Germanium to produce an excess of electrons, whereas a *p*-type 65 material has an excess of holes, or an electron deficiency. The area where these two materials meet is called the *pn*-junction. At the *pn*-junction, this disparity creates a concentration gradient that causes electrons to diffuse into the *p*-layer and holes to diffuse into the *n*-layer. This diffusion

results in an opposing electrical potential, often referred to as an internal bias. Charge carriers cannot reside in this region, therefore it is termed the depletion region.

In detector 35 of the present invention, light enters the device through a thin *p*-type layer. Absorption causes light intensity to drop exponentially with penetration depth. Any photons absorbed near the depletion region produce charge carriers that are immediately separated and swept across the *pn*-junction by the inherent internal bias of the device. Charge carriers created outside the depletion region will move randomly, many of them eventually entering the depletion region to be swept rapidly across the *pn*-junction. Some of them will recombine and disappear without ever reaching the depletion region. This movement of charge carriers across the *pn*-junction upsets the electrical balance and produces a small photocurrent that is detected at the electrodes of the detector. The electrical current or voltage produced is proportional to the light intensity incident on the detector 35.

Figure 5a, illustrates the response 72 of a typical detector 35 to a varying intensity 71 for a broadband signal. It can be seen by varying the intensity 71 of the light source will effect the bandwidth or the total response 73 of the detector 35. In particular by increasing the intensity 71 of the light source, the range of wavelengths 73 that can be measured at a particular time is decreased. Reducing the intensity 71 of the light source increases the range of wavelengths 73 that can be measured but only up to the maximum bandwidth response of the detector 72.

By increasing the intensity 71 of the light source 1, the Quantum efficiency of the detector is increased. The Quantum efficiency is defined as the ratio of the photocurrent in electrons to the incident light intensity in photons (or the sensitivity of the photodetectors to different wavelengths).

Referring to Figure 4a, short wavelengths 80 of light penetrate a short distance into the structure of the detector 35 ie. light will interact close to the surface of the diode. Referring to Figure 4b, longer wavelengths 81 of light penetrate deeper into the structure of the detector 35, or in extreme cases, the detector 35 becomes totally transparent to long wavelengths 81. Short wavelengths 80 of light are comprised of high energy photons while longer wavelengths 81 contain lower energy photons. The detector 35 only

produces a current or voltage at its electrodes if the photons absorbed have enough energy or are close enough to traverse the *pn*-junction. This effect is called the 'cutoff wavelength'.

Photons with a wavelength less than the cutoff and in close proximity with the *pn*-junction will produce current or voltage. Photons with a longer wavelength greater than the cutoff will not produce current or voltage.

In order to control the cutoff wavelength it is desirable to control the thickness of the depletion region 66. The easiest way to expand this layer 66 is to apply an external electrical bias (voltage) 68. By applying an external electrical bias 68, the *p*-type 65 and *n*-type 67 regions reduce in thickness so disabling some of the longer wavelengths 81 to create charge carriers. The thickness of these layers is directly controlled by the magnitude of external electrical bias 68. The greater the magnitude of external electrical bias 68, the thinner the region where charge carriers are formed 65 and 67 and the smaller the cutoff wavelength is. Ideally the control of the voltage 68 is provided by the microprocessor 3.

Figure 5b illustrates the incorporation of the external bias variable 68 to aid in the control of the detector 35. This external bias variable 68 is the magnitude of the external voltage 68 applied to the detector 35. As previously discussed, varying the voltage 68 varies the thickness of the region where charge carriers are formed 65 and 67 so effecting the response bandwidth of the detector 35. Specifically, by increasing the magnitude of the external voltage supply 68, the upper bandwidth response of the diode decreases 93. In the preferred embodiment of the present invention, the control of external voltage 68 is controlled by the microprocessor 3. In practice external voltage 68 applied to the detector 35 is changed in a stepwise manner. Alternately the external voltage 68 is changed in a continuous fashion.

By combining the control of the light source intensity 71 and the external voltage applied 68 to the detector 35 by the microcontroller 3, individual components from the sample signal can be determined. In practise, for every stepped change in the external voltage 68, a number of different intensities 71 are emitted from the light source 1. For every cutoff band selected 70 a new range of detectable spectra is observed. The band

sweep (due to bias voltage) and intensity sweep (due to light source) leads to a combined set of data points arranged across the full spectrum of the device under investigation. This way the characterisation of all the spectra under investigation is possible.

There are numerous embodiments in the process of analysing the spectral absorption of a material in a test sample. In one embodiment, a signal, for example the reference signal, is transmitted through the chopper wheel 33 to the detector 35. The controlling module, typically a microprocessor 3, selects a voltage to be supplied to the detector 35, controlling the width of the depletion region 66, and thus selects a predetermined bandwidth that the detector 35 will be sensitive to. The microprocessor 3 then varies the voltage supplied to the light source 1 thus varying the intensity of the broadband light signal. The detector 35 will send representative signals to the microprocessor 3. This data is then stored in the microprocessor until the test is finished. The changes in the level of voltage supplied to the detector 35, selects detection bandwidths. This process repeats until measurements have been performed at all preselected bandwidths. The entire process is repeated again for the next light signal, for example the light signal from the sample path.

In another embodiment of the present invention, one signal, for example the reference signal, is transmitted through the chopping wheel 66 to the detector 35. The microprocessor 3 selects the predetermined bandwidth that the detector 35 is sensitive to, performed by selecting the voltage level supplied to the detector 35. The microprocessor 3 then varies the voltage level supplied to the light source 1 thus varying the intensity of the light signal. The detector 35 generates representative signals that are transmitted to the microprocessor 3. The chopper wheel 33 then rotates and blocks the reference signal and allows the next signal to be transmitted, for example the sample signal. Again the microprocessor 3 varies the intensity of the light source 1 and the measured values are stored in the microprocessor 3. As the chopper wheel 33 rotates again there is a dark interval, this is known as the dark current. There is no light incident on the detector 35 but an inherent current will flow across the *pn*-junction of the photodiode. This current level is measured and used by the microprocessor 3 to calibrate for any temperature drift in the electronics.

The output signals from detector 35 are in the form of voltages, these are measured from the detectors 35 electrode terminals. These signals are representative of the light incident on the detectors 35 surface. The output signals are small, they are proportional to the amount of current flowing through the diode as a result light being detected. These signals are too small and are in the wrong format to be accurately detected by the microprocessor 3, so they are modified by output circuitry 6. This output circuitry 6 is comprised of two sections, namely an amplification section 7 and a conversion section 8. The amplification section 7 is comprised of an operational amplifier circuit. The gain provided by this circuit is dependant on the components used, therefore gain may be increased or decreased accordingly. Alternately other types of amplification circuit 7 may be used in a similar manner. Once the signal is amplified, it is converted from an analogue signal to a digital signal. This is performed either by a dedicated analogue-to-digital converter circuit 8 or in a analogue-to-digital converter contained within the microprocessor 3. The output signals from the detector 35 are now in a format that the microprocessor 3 can identify and use.

Signals from the detector 35 are continuously supplied to the microprocessor 3 as it is continuously measuring light incident on its surface. The microprocessor 3 takes discrete measurements from the continuously supplied signal and stores these signals in its memory.

The output of the detector 35, reflects the presence of material in a sample. Once the test is completed, the microprocessor 3 stores the measured values in an array in its memory.

Subsequent evaluation of these measured values may be made by a number of methods. Some trials and experimentation may be relied upon to determine the best method for obtaining values indicative of material presence in a sample. However, for ease of use, most embodiments will rely upon the comparison of received measured values with collected or stored data. This data may be values which have been pre-programmed into the microprocessor 3 so that the subsequent collection of initial set-up data by the user may not be required. This stored data may comprise of values typical for the type of samples to be analysed although it is envisaged for most embodiments that there will be

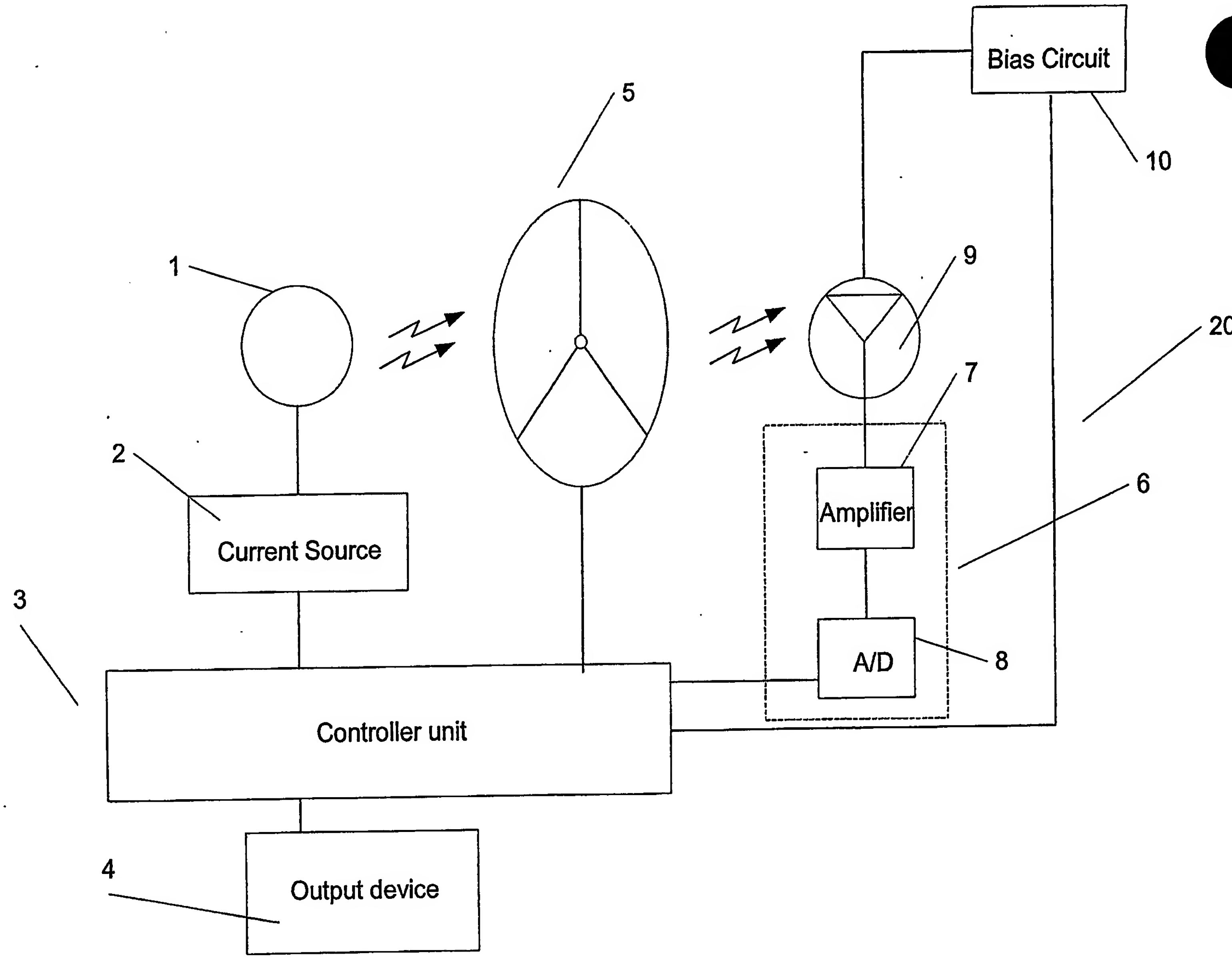
provided provision for routine calibration using reference samples either to check accuracy and/or adjust the apparatus. Calibration information will be stored in the microprocessor 3 or in software being run by the external processing means. The use of software may be more flexible allowing for the updating of software to change the performance of the apparatus. In addition, calibration data is updated whenever a new calibration is run.

After treatment of all calibration data with a multiple regression method, the correlation factor and the intercept or the free factor are obtained. Summation of this formula results in typically eight locations in the total calibration data array. These eight readings relate to the locations that provided the best measurements.

The spectral response, material size and density is obtained by the multiplication of each individual sample reading at the predetermined position in the array with its regression coefficient factor and addition of the free factor as shown in the following formula:

$$\text{Result} = \text{free factor} + \sum_{n=1}^{8} \text{coef}_n \,.\, \text{meas}_n$$

DATED THIS 13 DAY OF Sept 02
AJ PARK
PER S Herbert.
AGENTS FOR THE APPLICANT



1
2
Current Source
3
Controller unit
4
Output device
5
Bias Circuit
10
9
20
7
Amplifier
6
A/D
8

Figure 1

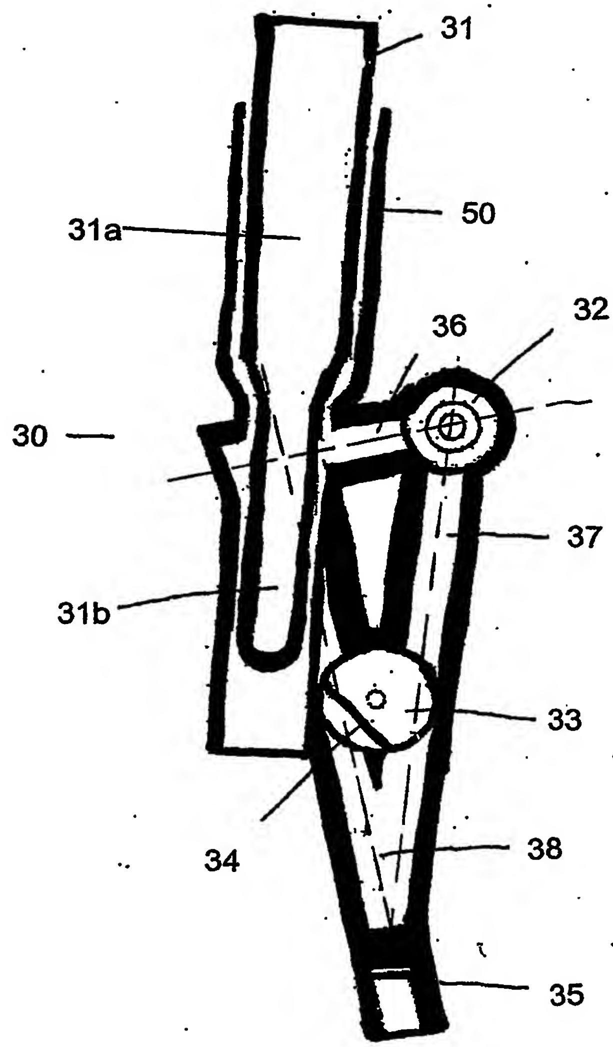


Figure 2a

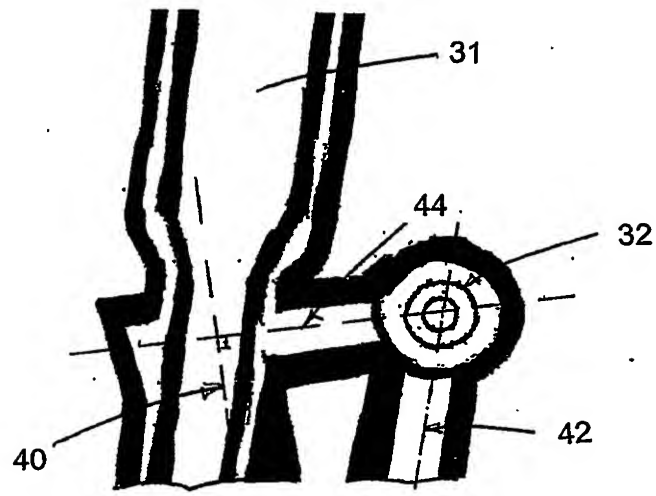


Figure 2b

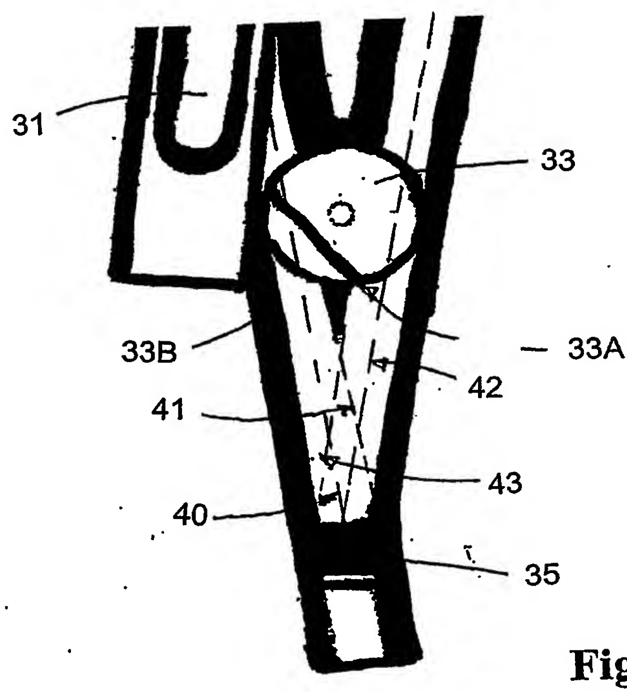


Figure 2c

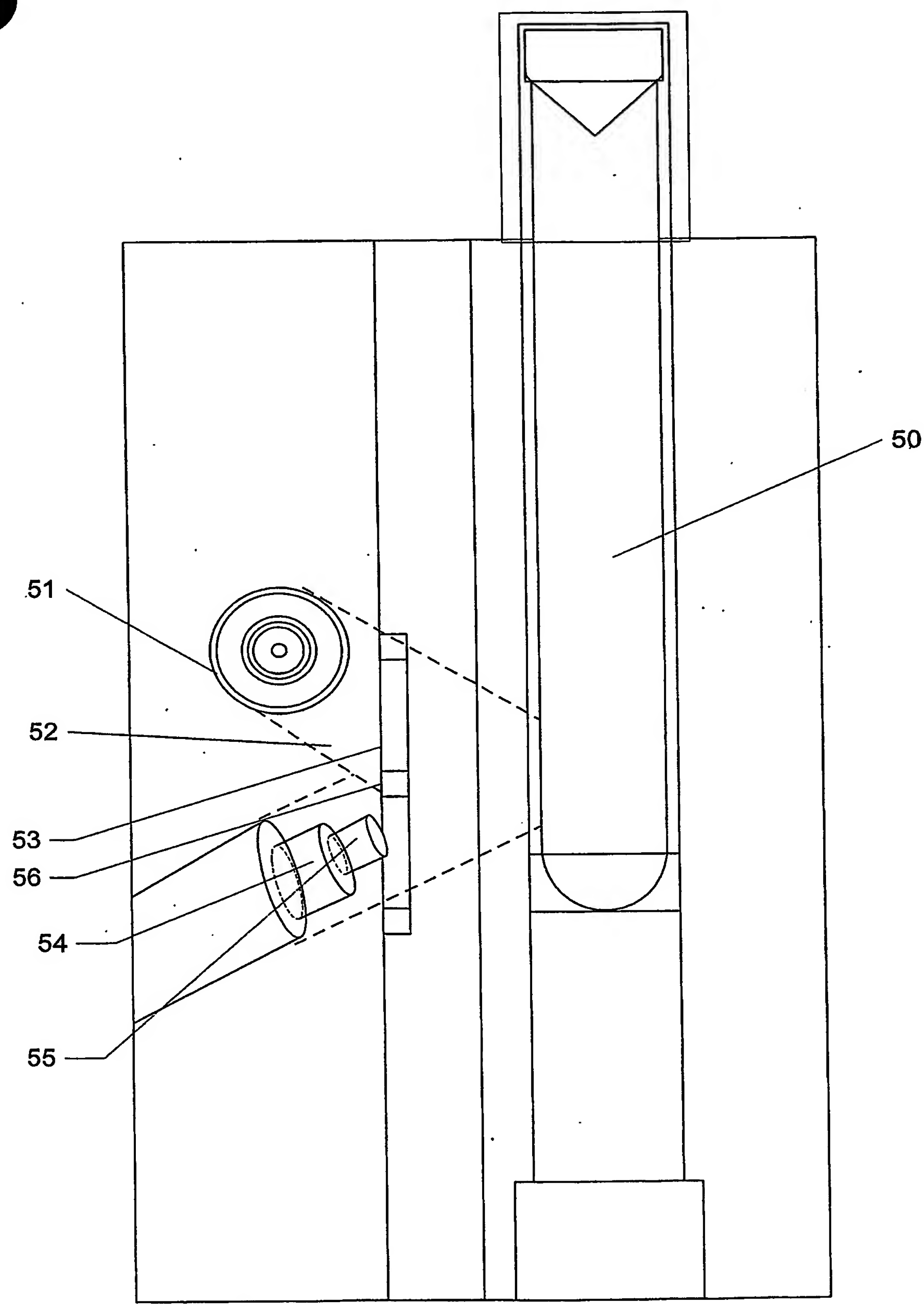


Figure 3 A

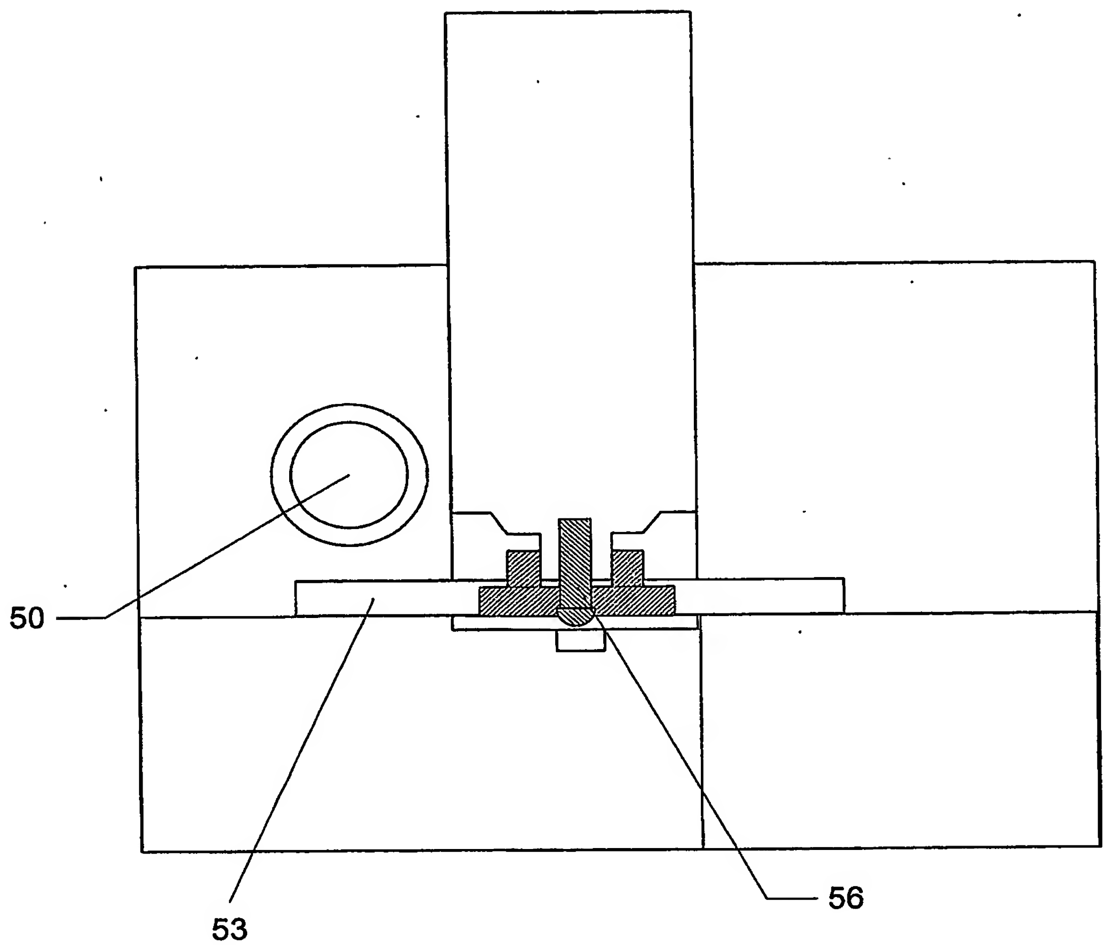


Figure 3 B

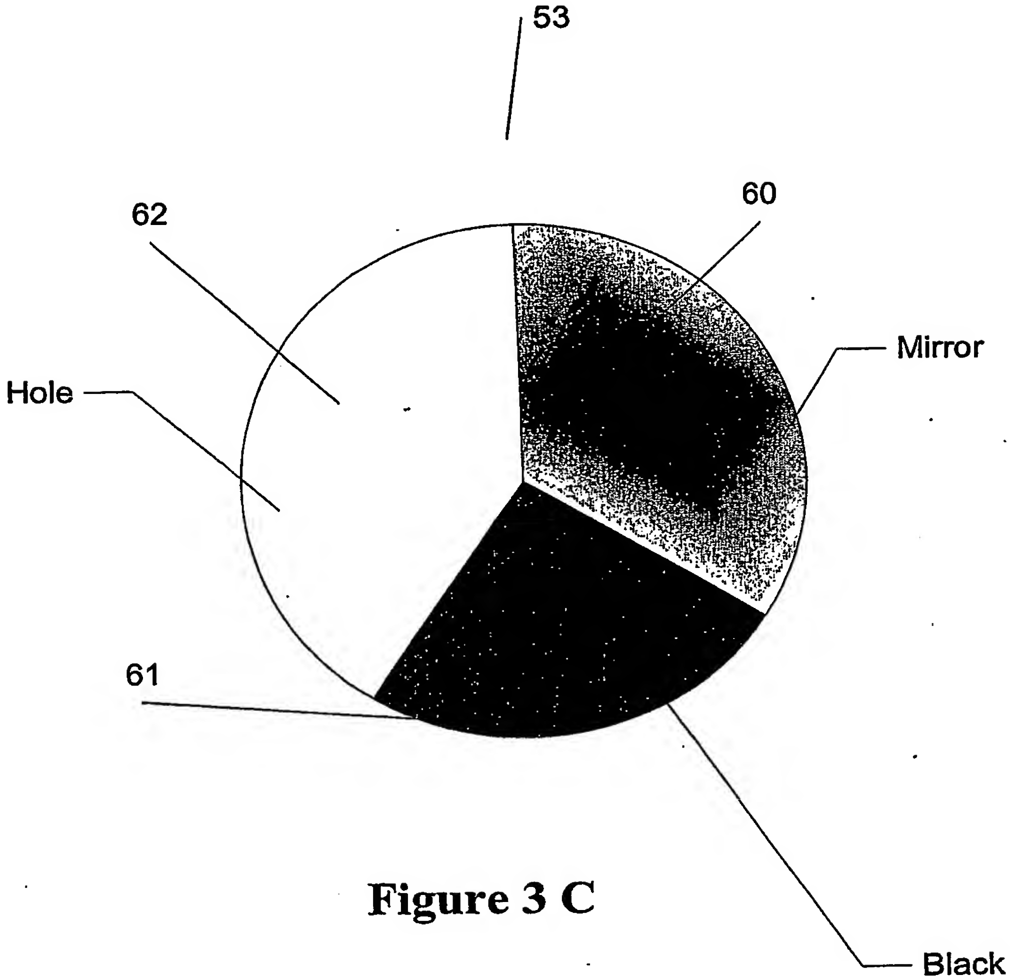


Figure 3 C

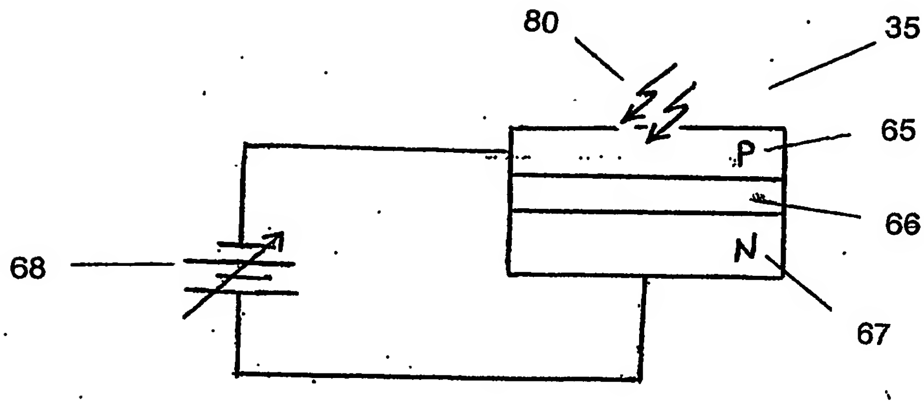


Figure 4A

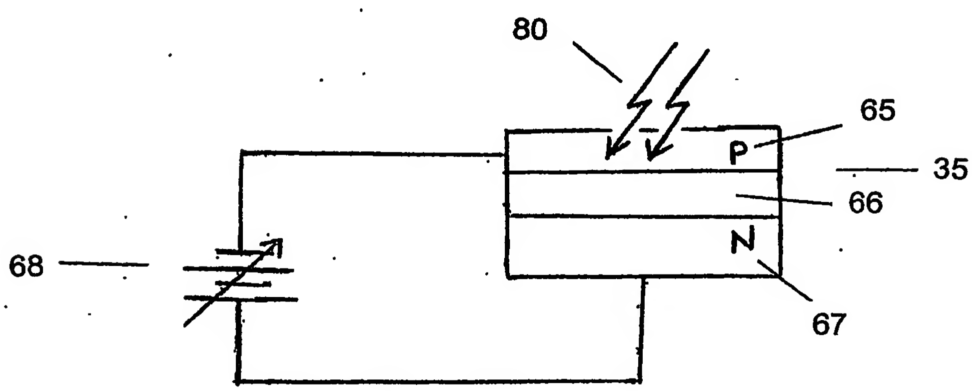


Figure 4B

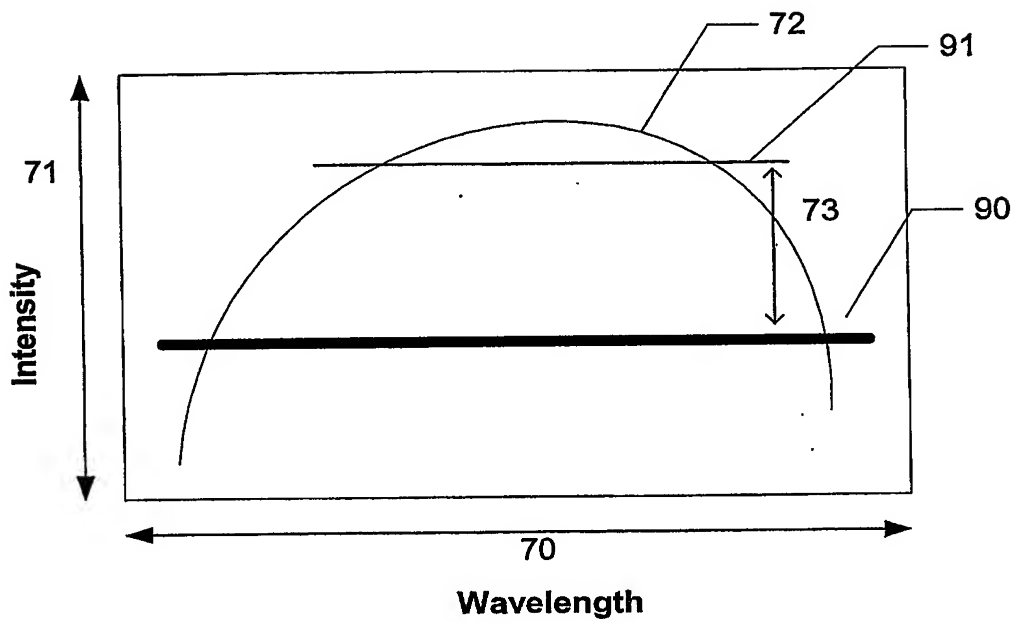


Figure 5A

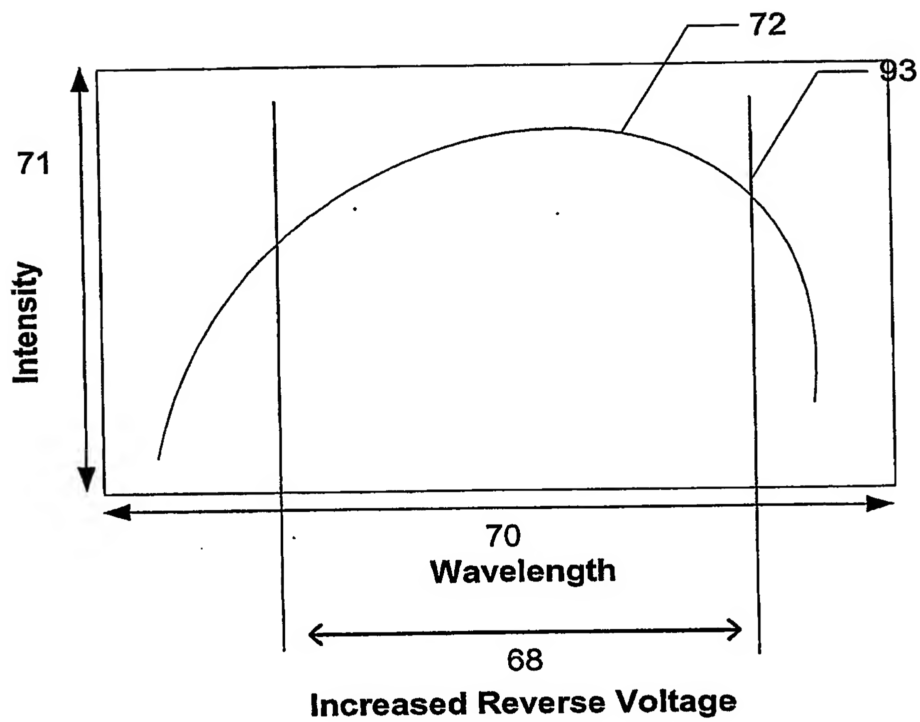

72
93
71
Intensity
70
Wavelength
68
Increased Reverse Voltage

Figure 5 B

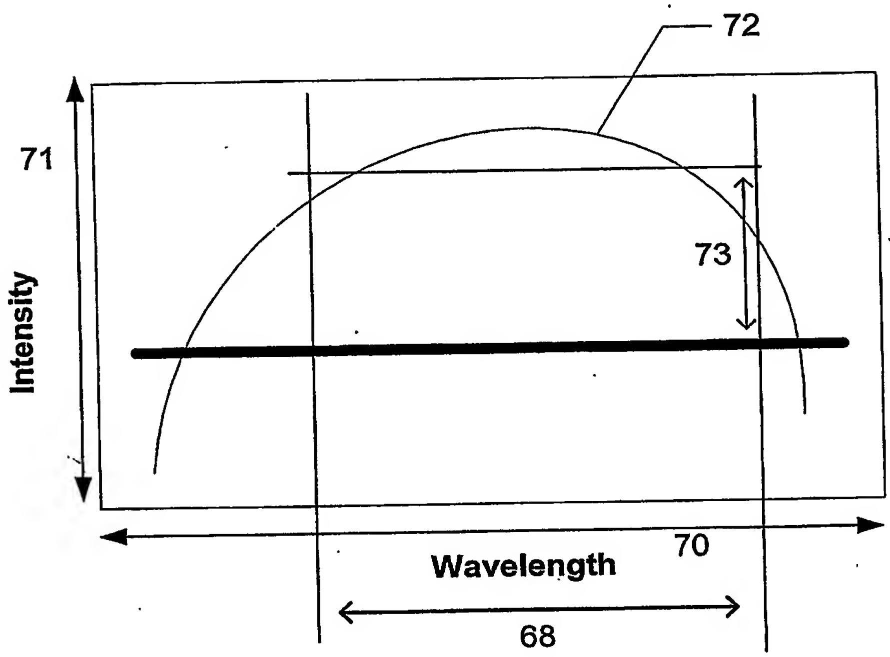


Figure 5 C